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# FT-IR Study of $N_2$ Adsorption on ZnO and HgO Modified Na-Y Zeolite Adsorbents

**Chieng, Y. Y.**[1] **Kamarudin, K. S. N.**[1] **Hamdan, H.**[2] **Mat, H. B.**[1]

[1]*Advanced Process Engineering (APEN) Research Group, Faculty of Chemical and Natural Resources Engineering,*
[2]*Zeolite and Porous Material Group, Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.*
*Corresponding author email address: hbmat@utm.my*

## Abstract

*FT-IR was used to study in situ gas-zeolite surface interactions and adsorbed species formed on ZnO and HgO modified Na-Y zeolites under ambient temperature (298 K). A general correlation between the integrated absorption band areas and the positions of $\nu_{N\text{-}N}$ bands interacting with the active adsorption sites on modified Na-Y zeolites are discussed. Results clearly demonstrate that the FT-IR bands of $N_2$ adsorbed on ZnO and HgO modified Na-Y zeolite was governed not only by the properties of adsorbate but also by the nature and strength of the active adsorption sites present on the zeolite surfaces. In general, blue-shifted $\nu_{N\text{-}N}$ bands are obtained relative to the gas-phase Raman frequency, which are due to the different adsorption behavior of these adsorbed molecules with end-on orientation on the active adsorption sites. In addition, the adsorbing molecules interact strongly with the surface at initial stage. The strength of these interactions will then decrease as adsorption active sites are fully occupied.*

**Keywords:** FT-IR, ZnO and HgO modified Na-Y zeolite, Adsorption, Nitrogen, Interaction.

## Introduction

In the last two decades, pressure swing adsorption (PSA), vacuum pressure swing adsorption (VPSA) and temperature swing adsorption (TSA) technologies have been continuously developing for gas nitrogen separation [1-5]. One of the most important scale processes is the separation of air to obtain nitrogen and oxygen [6-8]. As gas adsorbent, zeolite Na-Y microporous material with very unique physical structure and large internal surface area shows a good physical-chemical property that is suitable to use as nitrogen adsorbent in industry [9]. Apart from presenting attractive adsorptive and catalytic properties [10], Na-Y zeolite adsorbent as parent support exhibited higher efficiency in the high temperature and high-pressure gas separation processes [11-13].

On the other hands, many applications have been found for ZnO and HgO in recent years as catalyst [14-17], gas sensor [18-21], semiconductor [22-23] and superconductor materials [24-27]. Both of these metal oxides exhibited good porosity, selectivity and thermal stability properties. They also have been widely developed for industrial adsorbents [28-29]. Therefore, the well dispersion of ZnO and HgO into or onto the surface of Na-Y probably would modify zeolite properties such as the acidity, framework composition, as well as its gas nitrogen adsorption characteristics. Subsequently, it was the aim of this presentation to carry out extensive and detail FTIR experimental study on ZnO and HgO modified Na-Y adsorbents for gas $N_2$ adsorption. The fundamental mechanisms of interaction within adsorbate and the metal oxides modified zeolite Na-Y would facilitate the understanding of adsorption phenomena that leading toward the development of gas adsorbent with higher adsorption capacity and selectivity.

## Materials and Methods

### *Materials*

Commercial synthetic zeolite Na-Y (Si/Al = 2.88) was selected and used as support or parent material for the dispersion of ZnO and HgO. It was purchased from Zeolyst International Corporation (CBV 100, Lot number 10003101171). Meanwhile, the commercial powder metal oxides, HgO (99%, Acros Organics) and high purity commercial powder metal nitrates, $Zn(NO_3)_2.6H_2O$ (>99%, Merck) were employed as metal oxide powder and precursors, respectively to modify zeolite Na-Y system. Nitrogen (high purity grade, 99.995%) used was supplied by Linde Gas Singapore PTE LTD.

### *Preparation of Metal Oxide Modified Zeolite Samples*

Zeolite Na-Y (surface area of 820 $m^2/g$) was extensively mixed in a mortar with powdered HgO for 20 minutes at ratio up to 290 μmol/g adsorbent. The resulting mixture

was sieved to particle sizes of 300 μm and consecutive calcined at elevated temperature with heating rates of 10 K/min to 673.15 K in a furnace for 24 hours. Meanwhile, zinc nitrate was used as zinc oxide precursor solution for impregnation. For this purpose, 9 ml $Zn(NO_3)_2.6H_2O$ was kept under mild stirring for 2 hours with 3 g of Na-Y zeolite. The resulting mixtures were evaporated to dryness at room temperature followed by drying overnight at 383.15 K in oven. After that, the adsorbents were activated by calcination at 823.15 K (heating rates of 2 K/min) in furnace for 5 hours.

*Analytical Procedures*

A laboratory-made FTIR cell unit apparatus that made up of stainless steel equipped with a $CaF_2$ window is used. The adsorbent powders were pressed into thin circular pellet, which then placed in the FTIR cell apparatus. The FTIR cell was then connected to a vacuum-adsorption apparatus with a pressure below $10^{-3}$ mbar. Prior to the gas adsorption measurements, the samples were activated for 2 hours calcination at 673.15 K. The sample was then cooled down to room temperature and consecutively introducing the nitrogen into the FTIR cell at 138 kPa for 2 hours equilibrium adsorption measurement. The spectrums (10 scans) were recorded with a resolution of 4 $cm^{-1}$. The IR spectrum of adsorbed gases on HgO/Na-Y sample was then analyzed at pressures ranging from 34.5 kPa to 275.8 kPa. The areas under the peak corresponding to the physically adsorbed adsorbate species were then determined, correlated with the corresponding adsorbed amounts and energy of the interactions.

## Results and Discussions

In situ FTIR spectroscopy is a powerful tool for studying the adsorbed species interaction with zeolite directly and the transport of interacting molecules in micropores of zeolites and modified zeolite system [30]. In this study, adsorptions of $N_2$ on Na-Y zeolite and metal oxide modified zeolites were studied by transmission FTIR spectroscopy carried out at room temperature. The background spectrum, obtained after activation of the samples at 673.15 K for 2 hours before adsorption of gas, was subtracted in each case. Hence, all of the FTIR spectra obtained are the result of the interaction of gas with the adsorbent surface only.

Non-polar gas $N_2$ having very weak base property would only interact with strong acid sites in zeolite. Vibration of homomolecular diatomic nitrogen is infrared inactive in the gas phase [31]. However, adsorption in zeolite cavities would reduce the molecular symmetry of the molecules and results in the appearance of interaction in FTIR spectra [32-34]. In the present study, $N_2$ adsorption (equilibrium pressure was fixed at 138 kPa) was carried out at 298.15 K on ZnO and HgO modified Na-Y zeolite. The N≡N stretching vibrations of the molecules adsorbed on Lewis acid centers fall in the region of 2360 – 2320 $cm^{-1}$. For all samples, a main absorption band is observed at 2340 - 2350 $cm^{-1}$, which can be assigned to N≡N stretching vibration in the $N_2$ molecule adsorbed on the metal cation species that existed on the zeolite surface. These metal cations such as $Na^+$, $Al^{3+}$, $Zn^{2+}$ or $Hg^{2+}$ that dispersed on zeolite surfaces. The appearance of such a FTIR band indicates a strong interaction between the $N_2$ molecule and metal cation species.

The FTIR spectra of $N_2$ adsorbed on Na-Y and Group II B metal oxides modified samples (in the region 2320 –2360 $cm^{-1}$) are shown in Figure 1. The spectrum of Na-Y (a) shows absorption bands with maximum at 2332 and 2347 $cm^{-1}$, respectively. The appearance of weak band at 2332 $cm^{-1}$ was assigned to polarization of $N_2$ molecules adsorbed on $Na^+$ site, while strong band observed at 2347 $cm^{-1}$ was assigned to the vibrations of nitrogen bound to aluminum cation Lewis site [35]. It was noted that the $\nu$(NN) is upward shifted with respect to the gas phase (Raman spectra at 2330 $cm^{-1}$) with blue shift 2 $cm^{-1}$. The positive shift of the $\nu$(NN) was always observed when these molecules are axially perturbed by an electric field generated by a adsorption site with positive character.

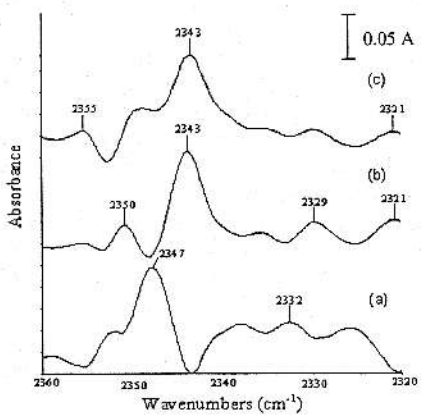


*Figure 1 - FTIR spectra of $N_2$ dosed on (a) Na-Y; (b) ZnO/NaY; and (c) HgO/NaY at 298 K and equilibrium pressures fixed at 138 kPa.*

For zinc oxide and mercury oxide modified zeolite Na-Y (spectra b to c), an asymmetrical contour with a peak at region 2340 - 2360 $cm^{-1}$ is observed of N-N vibrations at 138 kPa equilibrium pressure. This band can be assigned to N-N vibrations in the complexes with Lewis acid sites ($Zn^{2+}$ and $Hg^{2+}$) of samples. The peaks at 2332 $cm^{-1}$ and 2347 cm-1 were found to decrease after the modification. It can be suggested that small amount of ion-exchanged process replacing the $Na^+$ and $Al^{3+}$ cations have been occurred during the modification. From the Si/Al ratio observation, both of the samples (Si/Al = 2.34) have decreased the aluminium cations up to 20 %. Somehow, the decrement of bands intensity at 2332 and 2347 $cm^{-1}$

wavelength might also due to the stronger interaction of nitrogen molecules to the zinc and mercury cations sites compared to unmodified Na-Y zeolite. Whatever is it, the position of N-N stretching mode Na-Y zeolite is retained; the addition of ZnO and HgO shifted the high frequencies bands from 2347 $cm^{-1}$ to 2343 $cm^{-1}$. These spectrums showed evidence that ZnO and HgO in the same group have been successively dispersed on Na-Y surfaces and give influences on nitrogen adsorption mechanisms. In addition, the position of $\nu$N-N component at higher frequency after the adsorption process compared to free gas phase molecules indicated the end-on position of nitrogen molecules adsorbed on the active sites.

Generally, the main difference of $N_2$ adsorption bands for different types of metal oxides modified Na-Y is the peak areas corresponding to the physically adsorbed species. At 298 K and 138 kPa adsorption condition, the strength and amount of gas adsorption could be predicted from the increase of absorbance area in the FTIR spectrum. In other words, the areas of the absorption bands at specific region are proportional to the molar of adsorbed amounts. The column chart as illustrated in Figure 2 indicated that the dispersion of ZnO and HgO on Na-Y zeolite caused the enhancement of gas nitrogen adsorption capacity. Mercury oxide modified Na-Y shows more pronounces effect compared to zinc oxide. Therefore, the changes of the size metal cations and acidity properties in Group IIB metal oxides is projected to the leapt in nitrogen adsorption capacity.

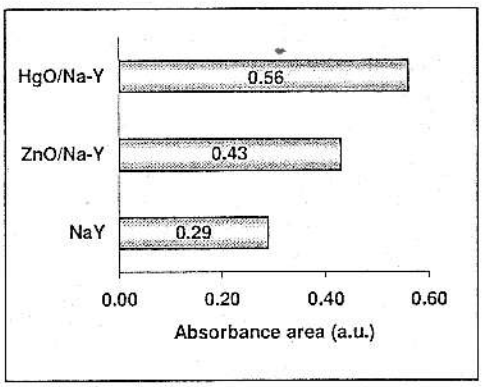


*Figure 2 – The corresponding areas of the FTIR spectrum peak at (2355 – 2320 $cm^{-1}$ region) for nitrogen adsorption at 298 K and 138 kPa of adsorbents studied.*

The temperature and pressure of adsorption are also the key factors that give influences to the adsorbates adsorption mechanisms. The temperature of adsorption will not be discussed here due to the constraint of apparatus condition. The effect of equilibrium pressure to the mechanism of $N_2$ interaction with zeolite surfaces were studied at room temperature (298 K) with increasing pressure on HgO modified zeolite Na-Y as shown in Figure 3. The integrated absorbance of the stretching bands changed with the pressure, but the band frequencies almost unchanged. Briefly the spectra show, at the lowest pressure 34 kPa, only one symmetric band at 2348 $cm^{-1}$ was detected and attributed to linear $Hg^{2+}$- $N_2$ species. The physically adsorbed nitrogen species shows weak interaction with HgO modified Na-Y zeolite surfaces. An increase of the equilibrium pressure resulted in an increase of the intensity and development of a new band at 2343 $cm^{-1}$ which was assigned to $Hg^{2+}(N_2)_2$ germinal complexes. The formation of germinal species means more gas nitrogen molecules are adsorbed on adsorbents surfaces. In certainty, the strength of adsorbate-adsorbent interaction is increased gradually. At the highest pressure (spectra e), the two bands intend to form a nearly symmetric envelope, accompanied by broadening and intensity decrement that evident in Figure 4.

It is suggested that at the saturation condition, the active adsorption sites on the surfaces of adsorbents have been fully covered by the physically adsorbed nitrogen species. Thereby, decrease the interaction energy within the adsorbates and adsorbent. Moreover, it is observed that the peak area in the 2340 – 2352 $cm^{-1}$ region is remained almost constant when the equilibrium pressure 138 –207 kPa is applied to the adsorption system. By further increment of high equilibrium pressure to 276 kPa, resulted in the decrease of absorbance area dramatically to 0.43 arbitrary units. The HgO modified Na-Y adsorption performance at room temperature is therefore expected to reach the saturation condition at 207 kPa equilibrium pressure.

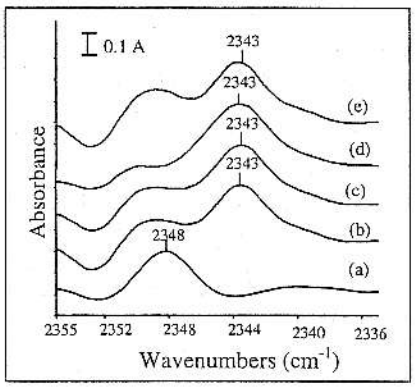


*Figure 3 - FTIR spectra of $N_2$ adsorbed on HgO/Na-Y at 298 K with equilibrium pressure (a) 34 kPa; (b) 69 kPa; (c) 138 kPa; (d) 207 kPa and (e) 276 kPa.*

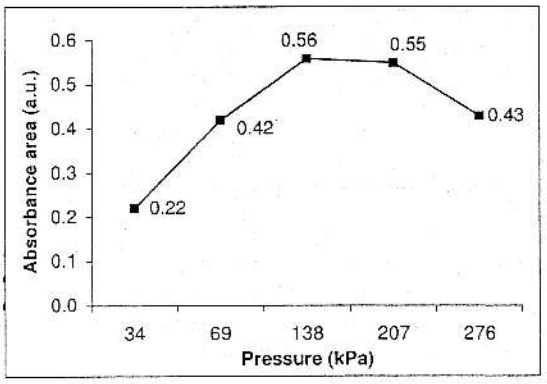


*Figure 4 - Effect of equilibrium pressure to the IR absorbance areas (2340 – 2352 $cm^{-1}$ region) and gas $N_2$ adsorption characteristics*

The salient point of the results obtained regarding on $N_2$ and adsorbent interaction can be explained as strong interaction of adsorbate-adsorbent happens initially for metal oxide modified zeolite in which their pore size and surface chemical composition have been varied through the oxide dispersion. The strength of these interactions will then decreases (absorbance areas) as these specific sites are occupied or reached the saturation capacity. Thereinafter, the understanding and well controlled of parametric effects on metal oxide dispersion as well as the temperature and pressure of adsorption are very important to manipulate the adsorptive properties of adsorbents for the enhancement of nitrogen adsorption.

## Conclusion

The adsorptions of nitrogen on metal oxides (Lewis sites) are differing in nature and strength from the acid sites of unloads zeolite. Different types of metal oxides even in the same Group II B caused different orientation and band shapes of N≡N interaction with metal species. Mercury oxide modified Na-Y zeolite shows the most promising potential as excellent gas nitrogen adsorbent. The understanding of adsorbate-adsorbent interaction on ZnO and HgO modified Na-Y leads toward the development of vast applications for industrial significance.

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